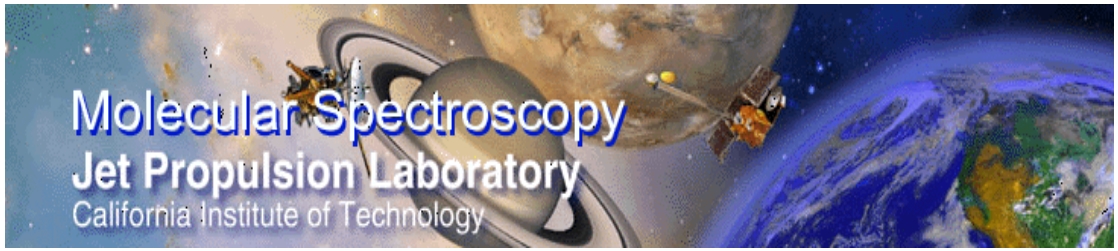
Millimeter-wave Chirality Spectrometer (ChiralSpec)

Shanshan Yu, Theodore Reck, John Pearson, Michael Malaska and Robert Hodyss

Jet Propulsion Laboratory, California Institute of Technology, USA

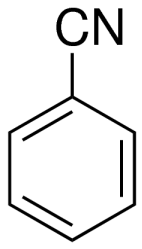
Brooks Pate

University of Virginia, Charlottesville, VA 22903, USA

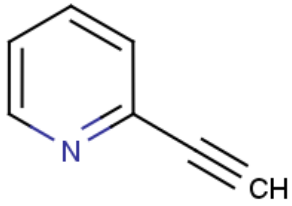


Overview of ChiralSpec

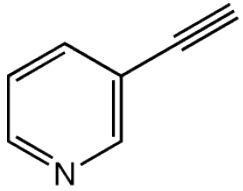
- **Instrument description**: a simple mm-wave spectrometer operated in two modes:
  - Chirality detection mode to determine which enantiomer is in excess
  - Survey mode as a traditional mm-wave spectrometer to characterize chemical composition
- **Chirality detection theory formulated in 2012 by Hirota** and experimentally demonstrated by groups in Harvard and Virginia at 2-18 GHz with large instruments
- **Goal of this effort**: experimental demonstration of chirality detection at 75-205 GHz where there is a path for instrument miniaturization.
- **Addresses planetary science objectives** by looking for **biosignature patterns** : chirality of amino acids; double-bond position in fatty acids; amino acids distribution, etc.
- **Complimentary to mass spectrometer for distinguishing isomers of the same molecular weight**, e.g., C_7H_5N, 103 Da, interesting to Titan, where is N inserted to? What is arrangement of atoms?



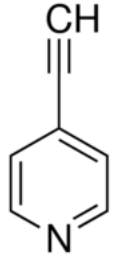
Benzonitrile



2-Ethynylpyridine



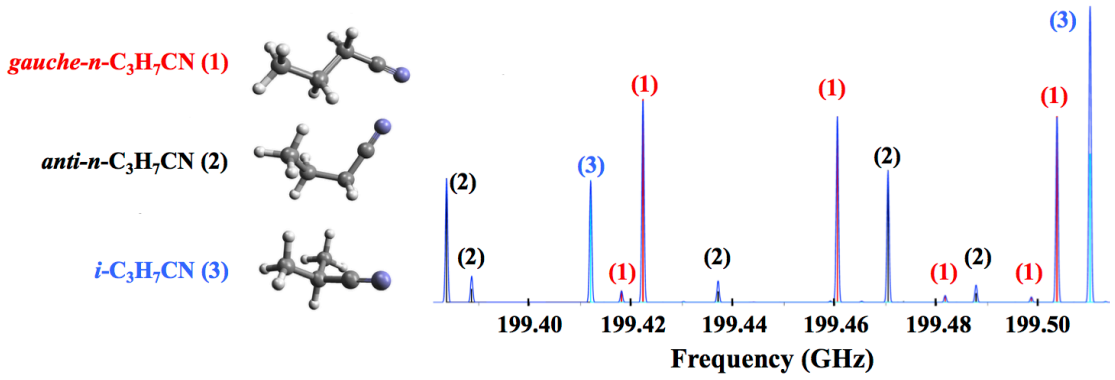
3-Ethynylpyridine



4-Ethynylpyridine

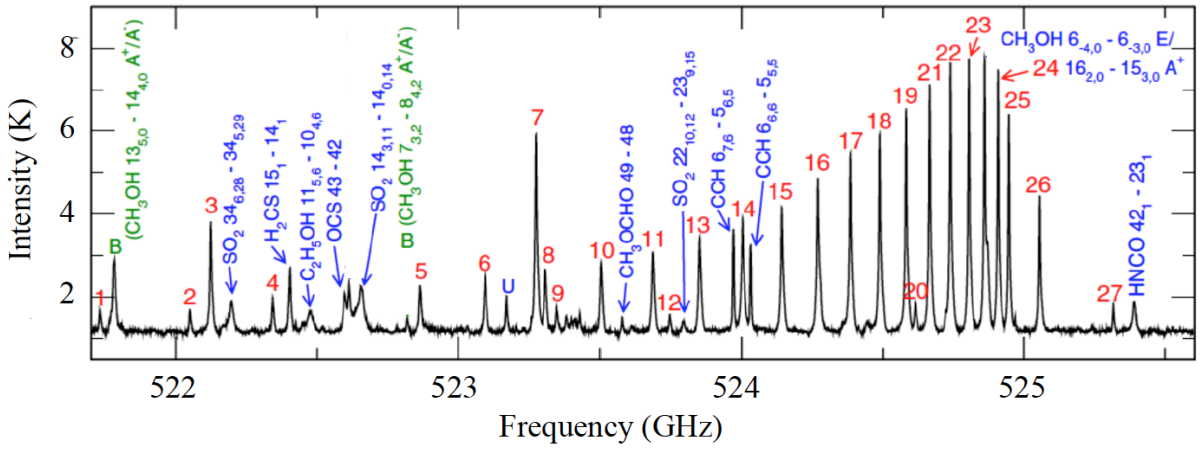
ChiralSpec's core: rotational spectroscopy

- Non-invasive approach
- Extraordinary capability of distinguishing isomers via high resolving power



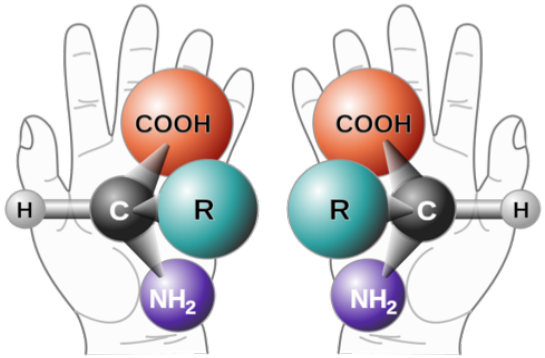
Multiple separate lines from each isomer ensure secured identification

- Capable of analyzing mixture of gases without separating them first



Survey spectrum of Orion KL from Herschel/HIFI (red numbers label CH3OH)

What is Chirality?



- Enantiomers of a chiral molecule: non-superimposable mirror images
  - Referred in terms of right- and left-handedness
  - Identical in many properties making them challenging to distinguish
  - Indistinguishable by mass spectroscopy
- Can be used as a chemical 'biomarker' for search for life
  - Organisms on Earth use predominately homochiral molecules
  - Life uses only left-handed amino acids
  - Life used only right-handed sugars

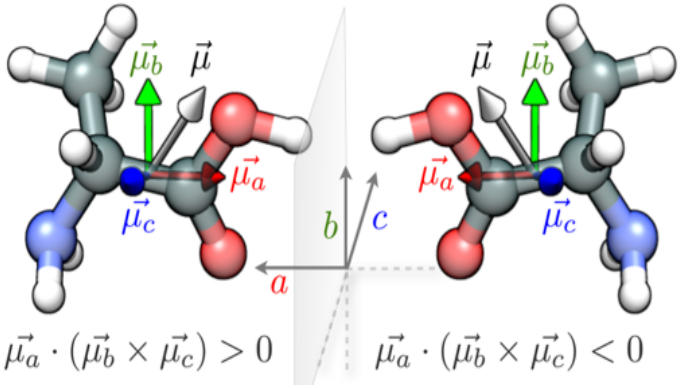
Image source: http://www.nai.arc.nasa.gov

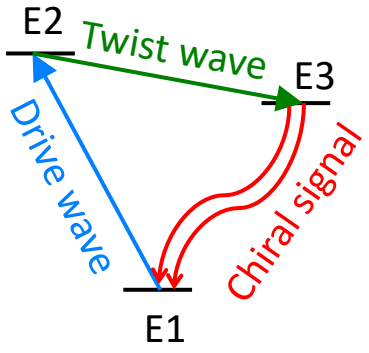
Comparative Technologies

Technology	Methodology	Sensitivity	Comments
ChiralSpec	Rotational spectroscopy Targets in gas phase	Gas: 10^9 molecules/cm^3 with 1L volume Solid: ppm level with 0.2mg sample	Not require derivatization Insensitive to non-polar molecules
GC-MS	Gas chromatography Targets in gas phase	ppm	Require derivatization
MILA	Laser induced fluorescence Targets in aqueous phase	Liquid: 100 pM (10^{-10} mol/L)	

- Gas chromatography (GC), implemented in Rosetta/COSAC and Curiosity/SAM
- Microfluidic Life Analyzer (MILA)
  - Capillary electrophoresis-based laser induced fluorescence (CE-LIF)
  - Developed with PICASSO-13 (PI Peter Willis of JPL)
  - With focus on amino and carboxylic acids
  - Measurements involve liquid extraction of samples, fluorescent tagging, introduction of two chiral recognition agents

Principle of chirality detection by ChiralSpec

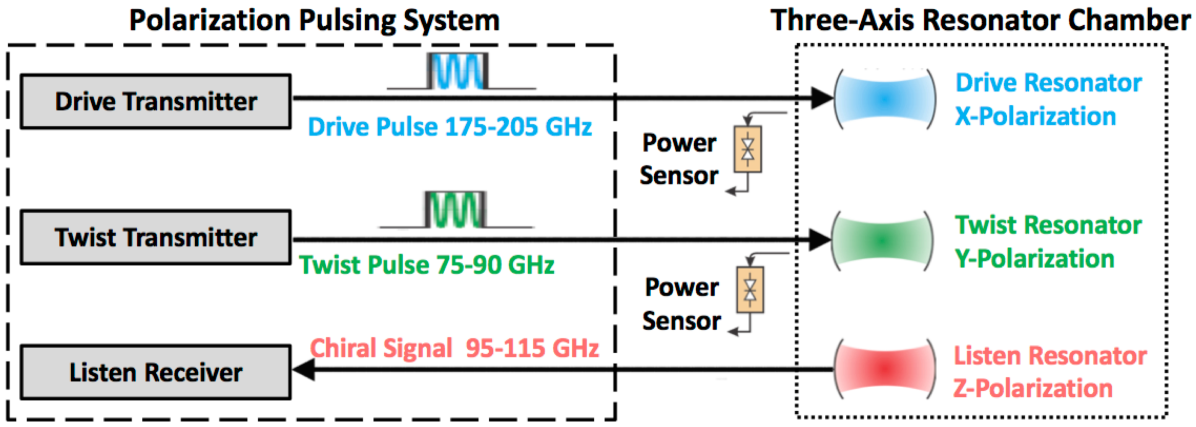


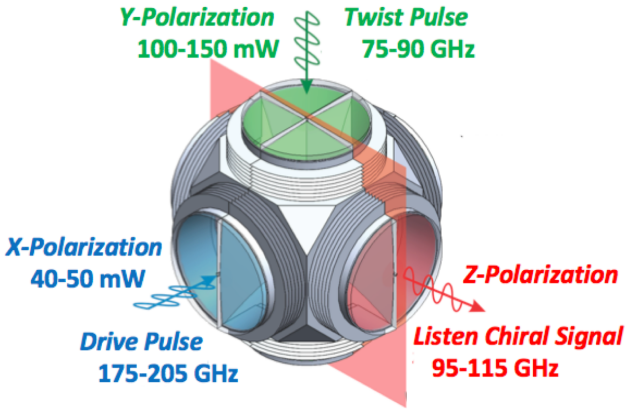


(molecular energy level)

- ✓ Exploiting **opposite signs of dipole moment products** (Image : Shubert et al 2016)
- ✓ Simultaneously using a cycle of three transitions involving the *a*, *b* and *c* dipoles
- ✓ Generating a time-domain chiral emission signal via exciting species with two pulses
- ✓ Enantiomeric pair's chiral signals: same frequency but **180^{o} phase difference**

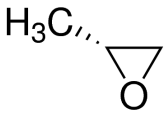
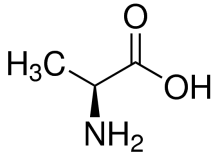
Schematic of ChiralSpec instrument





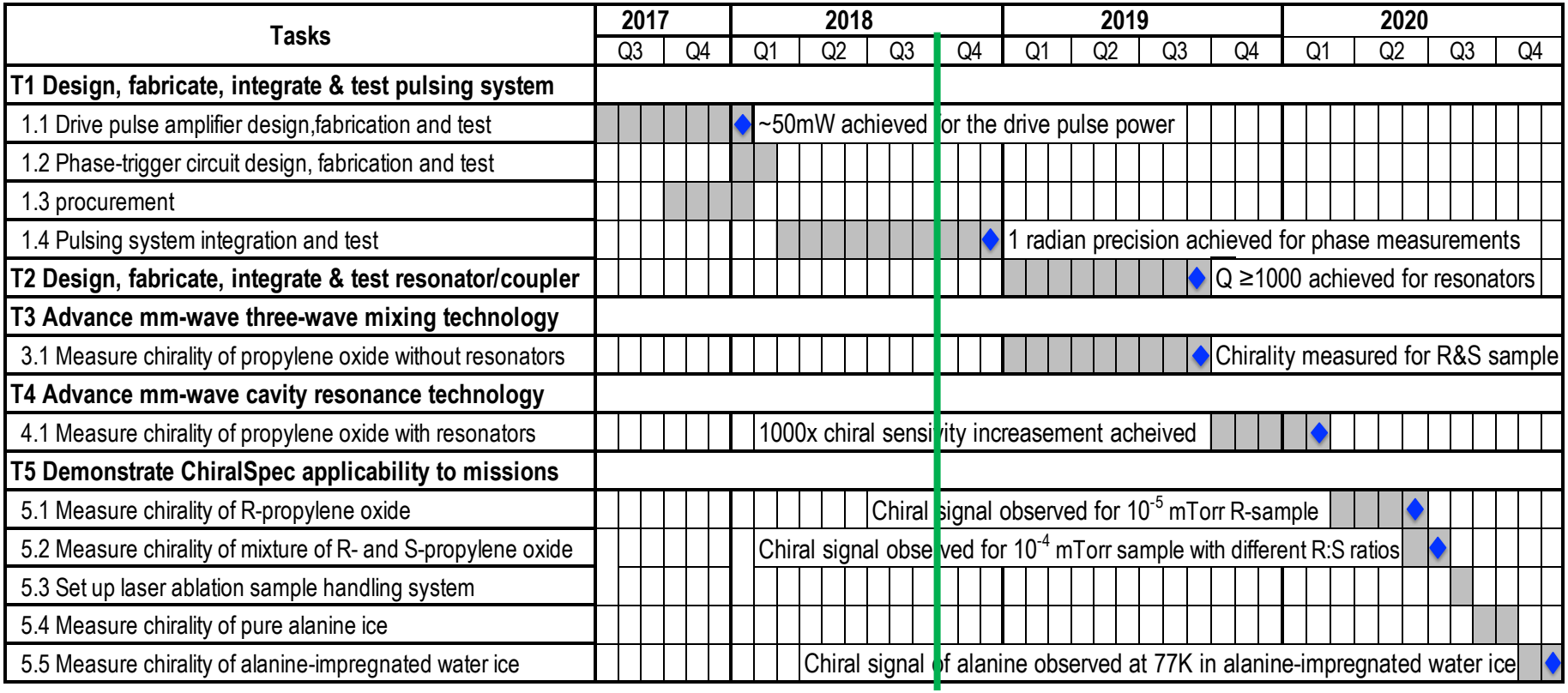
- All three waves capable of tuning frequencies in wide ranges
  - Capable of tuning to molecular fingerprint frequencies
  - Capable of **analyzing mixture of gases without separating them first**
- Chirality detection mode with all three waves on
  - Enantiomeric pair's chiral signals: same frequency but **180° phase difference**
  - Giving **difference abundance of enantiomeric pair**
- Survey mode with one wave on
  - Giving **sum abundance of enantiomeric pair**
  - Giving abundance for each of nonchiral molecules

Benchmark Molecules

Molecule	Cycle	Pulse	Transition	Freq. (GHz)
Propylene Oxide (CH_3CHCH_2O) MW=58 g/mol μ_a, μ_β, μ_c =0.95,1.67, 0.56 Debye 	1	Drive	$8_{4,4} \leftarrow 7_{3,4}$	182.856
		Twist	$8_{3,5} \leftarrow 8_{4,4}$	81.256
		Listen	$7_{3,4} \leftarrow 8_{3,5}$	101.599
	2	Drive	$15_{4,11} \leftarrow 14_{4,10}$	191.226
		Twist	$14_{5,10} \leftarrow 15_{4,11}$	88.069
		Listen	$14_{4,10} \leftarrow 14_{5,10}$	103.157
Alanine (CH_3CHNH_2COOH) MW=89 g/mol μ_a, μ_b, μ_c =0.62, 1.33, 0.34 Debye 	1	Drive	$21_{17,4} \leftarrow 20_{16,4}$	191.590
		Twist	$21_{16,5} \leftarrow 21_{17,4}$	76.855
		Listen	$20_{16,4} \leftarrow 21_{16,5}$	114.735
	2	Drive	$20_{19,1} \leftarrow 19_{18,1}$	195.558
		Twist	$20_{18,2} \leftarrow 20_{19,1}$	86.643
		Listen	$19_{18,1} \leftarrow 20_{18,2}$	108.915

- Propylene oxide is the first chiral molecule observed in ISM (McGuire et al 2016), is volatile and easier for sampling handling (vapor pressure of 450 Torr at 300K).
- We will use laser ablation to bring alanine into gas phase.

Schedule and Milestones



Acknowledgements

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